

Fe K-edge EXAFS study of the crystal phase transition of highly oriented nanorod-arrays of ferric oxides

L. Vayssieres, J. Guo, J.-E. Rubensson, J. Nordgren (Uppsala University)

Beamline(s): X18B

Introduction: The quest for cheap and reliable metal oxide materials for photovoltaics applications has resulted in the design of highly oriented three-dimensional array of hematite nanorods. Such purpose-built material consists in nanorods of about 3 nm in diameter, bundled as 50 nm nanofibers and oriented parallel or normal to the substrate¹. It has been used to develop photovoltaic², photocatalytic³ cells as well as nanocomposite material⁴. Indeed, the diameter of the nanorods allows a perfect match with the minority carrier diffusion length of hematite. Accordingly, a very efficient photogenerated charge separation was obtained as well as a high incident photon to electron conversion efficiency of ca. 60% at 350 nm, which led to the creation of a 2-electrode hematite photovoltaic cells. Besides the well-designed direct, grain boundary-free, electron pathway and the excellent structural match with the hole diffusion length, a 2D quantum confinement has also been suggested to account for the unusual high efficiency of the hematite nanorod-array photoanode. Therefore, an EXAFS study at Fe K-edge appeared definitely necessary to obtain structural information at atomic level by probe the local environment of iron at different stages of the crystal phase transition.

Methods and Materials: The general concept and synthetic procedure is performed according to a general template-free thin film processing technique¹ and has been successfully applied for the growth of large arrays of highly oriented anisotropic metal oxides⁵. Iron(III) oxides thin films (akaganeite, hematite) are grown directly onto a substrate from aqueous ferric chloride salt at 95°C in such conditions that the thermodynamic stabilization of the oxyhydroxide structure (akaganeite) is obtained. Then a heat treatment in air is performed at various temperature (above 385°C according to DSC) to induce the crystal phase transition and obtain the nanorod-array of hematite⁶.

Results: This EXAFS study clearly highlights the critical effect of the temperature on the local symmetry of the iron(III) during the phase transition (fig.1) and has provided important evidences to understand the electron transport in the nanorod-array and will therefore contribute to a great extent to the optimization of the photoelectrochemical cells as well as the development of novel devices based on such materials.

Acknowledgments: This work was supported by the Swedish Natural Science Research Council (NFR), the Swedish Research Council for Engineering Sciences (TFR), the Goran Gustavsson Foundation for Research in Natural Sciences and Medicine. The experimental work at NSLS, Brookhaven National Laboratory was supported by the U. S. Department of Energy. Dr. Syed Khalid (BNL) is acknowledged for his technical assistance.

- References:** [1] L. Vayssieres, N. Beermann, S.-E. Lindquist, A. Hagfeldt, *Chem. Mater.* 13(2), 233-235 (2001).
 [2] N. Beermann, L. Vayssieres, S.-E. Lindquist, A. Hagfeldt, *J. Electrochem. Soc.* 147(7), 2456-2461 (2000).
 [3] L. Vayssieres, J.-H. Guo, J. Nordgren, *J. Nanosci. Nanotech.* 1(4) (2001) in press.
 [4] T. Lindgren, H. Wang, L. Vayssieres, A. Hagfeldt, S.-E. Lindquist, *Solar Energy Mat. Sol. Cells* 71 (2002) in press.
 [5] L. Vayssieres, J.-H. Guo, J. Nordgren, *Mater. Res. Soc. Symp. Proc. Vol. 704*, (2002) in press.
 [6] L. Vayssieres, J.-H. Guo, J. Nordgren, *Mater. Res. Soc. Symp. Proc. Vol. 635*, C781-786 (2001).

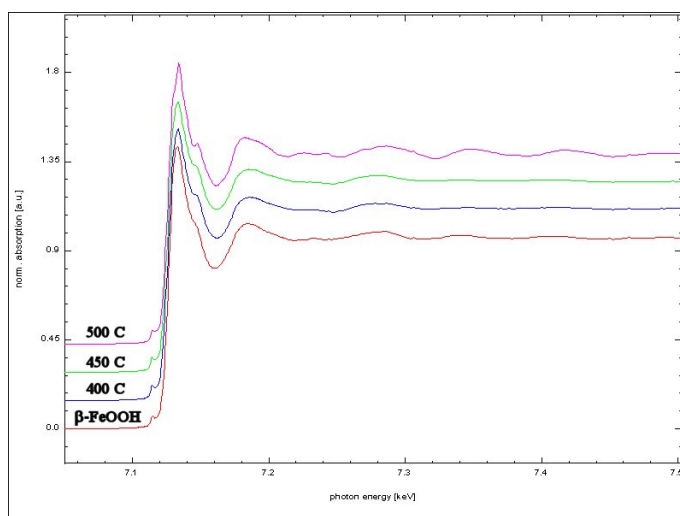


Figure 1. Fe K-edge EXAFS spectra of highly oriented nanorod array of β -FeOOH (akaganeite) at room temperature (bottom spectra) and after heat treatment at various temperatures yielding to the nanorod array of α -Fe₂O₃ (hematite).